

# PATENT SPECIFICATION

(11) 1 526 022

1 526 022

- (21) Application No. 1728/76 (22) Filed 16 Jan. 1976  
 (31) Convention Application No. 2 501 987  
 (32) Filed 18 Jan. 1975 in  
 (33) Fed. Rep. of Germany (DE)  
 (44) Complete Specification published 27 Sept. 1978  
 (51) INT CL<sup>3</sup> C08G 18/06  
 (52) Index at acceptance



C3R 32D11A 32D16B 32D16C 32D17 32D1 32D5 32D6C  
 32D6L 32D7 32D9B1 32E12 32E2A 32E2Y 32E3A  
 32E3B 32E3C1 32E3C2 32E3D 32E3E 32E3Y 32E4  
 32E6 32E7C 32E7D 32E7Y 32E8 32F1 32F2 32F5  
 32G2C 32G2Y 32G3X 32H5B2 32H5BY 32H8 32J1A  
 32J1X 32J1Y 32J2C 32J2D 32J2F 32J2X 32J2Y 32J3A  
 32J3Y 32J5 32J9A 32KC 32KH 32KJ 32S 32T2X C11  
 C12 C25 C33B L1B L2X L5D L5X L6G

## (54) MANUFACTURE AND USE OF CROSSLINKABLE THERMOPLASTIC POLYURETHANES

(71) We, BASF AKTIENGESSELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the manufacture of crosslinkable thermoplastic polyurethanes which contain at least two urethane groups, at least two urea groups, and at least two hydroxyl groups in side positions and to their use for the manufacture of curable coating compositions.

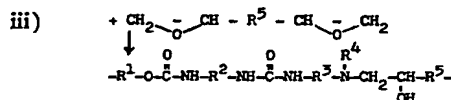
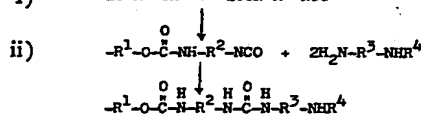
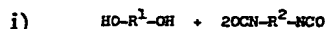
Coating compositions based on thermoplastic polyurethanes are known. They are distinguished by high elasticity and good adhesion to metal. However, since they only dry physically, their surface hardness is unsatisfactory, and their resistance to solvents is not as high as would be desirable.

The present invention seeks to provide a process for the manufacture of crosslinkable thermoplastic polyurethanes from which coating compositions having improved properties can be manufactured.

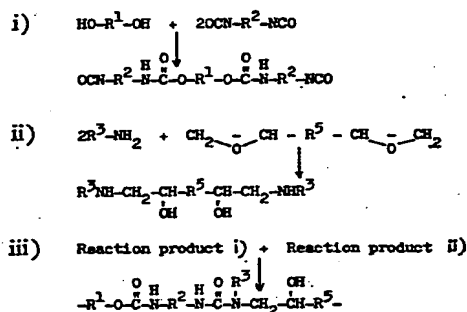
We have found that good results may be achieved in the manufacture of crosslinkable thermoplastic polyurethanes which have a molecular weight greater than 1,000, and preferably of from 5,000 to 100,000, and which contain at least two urethane groups, at least two urea groups, at least two hydroxyl groups in side positions, possibly in addition at least two tertiary amino groups, and, as end groups, secondary amino groups and/or epoxide or isocyanate groups by the use of either of two somewhat different 3-stage

methods which however belong to the same family.

1. In the first method, the first stage comprises reaction of a polyhydroxy compound A with a diisocyanate compound B, employing more than 0.5, preferably from 0.6 to 1, molecule of diisocyanate B per hydroxyl group of A. In a second stage, the resulting polyisocyanate is reacted with a diamine C.1 which carries a primary amino group and a secondary amino group, employing more than 0.5, preferably from 0.6 to 1, molecule of diamine per isocyanate group of the polyisocyanate. Finally, in a third stage, the resulting polyamine is reacted with a diepoxide compound D, employing sufficient diepoxide D to provide from 0.5 to 2 epoxide groups, and preferably about 1 epoxide group, of the diepoxide D per secondary amino group of the polyamine. The product produced contains at least two tertiary amino groups per molecule and secondary amino and/or epoxide end groups. The following set of equations illustrates a preferred embodiment where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>5</sup> are each a divalent radical and R<sup>4</sup> is a monovalent radical.



2. In the second method, the first stage comprises reaction of a polyhydroxy compound A with a diisocyanate compound B, employing more than 0.5, preferably from 0.6 to 1, molecule of diisocyanate B per hydroxyl group of A. In a second, independent, stage, an amine C.2 which carries a single primary amino group is reacted with a diepoxide compound D, employing sufficient amine to provide about one amino group of the C.2 per epoxide group of the diepoxide D. In a third stage, the polyisocyanate resulting from the first stage is reacted with the polyamine resulting from the second stage employing sufficient polyisocyanate to provide from 0.5 to 2 isocyanate groups, preferably about 1 isocyanate group, of the polyisocyanate per secondary amino group of the polyamine. The end product does not normally contain simple tertiary amino groups but its urea groups contain a tertiary nitrogen atom. The end groups are secondary amino groups and/or isocyanate groups. The following set of equations illustrates a preferred embodiment where  $R^1$ ,  $R^2$  and  $R^6$  are each a divalent radical and  $R^3$  is a monovalent radical.



Polyhydroxy compounds A which may be used for reaction with the diisocyanate compounds B in the first stage are dihydric and higher polyhydric saturated and unsaturated alcohols, and mixtures of such alcohols with one another or with minor amounts of monohydric alcohols. Examples of low molecular weight dihydric and higher polyhydric alcohols are saturated aliphatic and cycloaliphatic dialcohols, e.g. of up to 6 carbon atoms, for example ethanediol, propanediols, butanediols, hexanediols, neopentylglycol and cyclopentane-diol; unsaturated alcohols, e.g. hexenediol or butynediol; ether-diols and ester-diols, e.g. diethylene glycol, dipropylene glycol, hydroxy-pivalic acid neopentylglycol ester or the mono-ester reaction product of 1,3-propanediol and 3-hydroxy-propionic acid; and higher polyalcohols, e.g. trimethylolpropane, triethanolamine or pentaerythritol.

Examples of monoalcohols which also con-

tain other functional groups and which may be employed in minor amounts with polyhydric alcohols are mercaptoethanol, monomethylethanolamine and butanediol monoacrylate.

The following may be used as higher molecular weight polyhydroxy compounds, with molecular weights of from 600 to 5,000 and preferably from 800 to 3,000: hydroxyl-containing saturated or unsaturated polyesters (e.g. polybutanediol adipate), polyethers (e.g. polytetrahydrofuran), polyacetals, polycarbonates and polyacrylates, which latter may, e.g., contain hydroxyethyl acrylate, hydroxypropyl acrylate or hydroxybutyl acrylate as copolymerized units.

The use of a mixture of a low molecular weight polyhydroxy compound (molecular weight below 600) and a higher molecular weight polyhydroxy compound (molecular weight 600-5,000) is particularly advantageous.

The diisocyanate compounds B may be the compounds conventionally used in polyurethane chemistry. Aromatic, aliphatic or heterocyclic diisocyanates may be used, e.g. ethylenediisocyanate, ethylenediisocyanate, propylene-1,2-diisocyanate, 1,4-butanediisocyanate, 1,6-hexanediisocyanate, 1,8-octamethylenediisocyanate, m-phenylenediisocyanate, 2,4-toluylenediisocyanate, 2,6-toluylenediisocyanate, 3,3'-dimethyl-4,4'-diphenyldiisocyanate, 3,3'-dimethoxy-4,4'-diphenylmethanediisocyanate, 4,4'-diphenylmethanediisocyanate, 3,3'-dichloro-4,4'-diphenyldiisocyanate, 1,5-naphthylenediisocyanate, cycloaliphatic diisocyanates, e.g. hexahydro-1,3,5-trimethyl-2,4- and -2,6-diisocyanate and mixtures of these two isomers, 4,4'-dicyclohexylmethanediisocyanate, cyclohexane-1,4-diisocyanate, cyclohexane-1,3-diisocyanate and cyclohexane-1,2-diisocyanate, araliphatic diisocyanates, e.g. 1,3- and 1,4-xylylenediisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane and ester-diisocyanates of carboxylic acids, such as are described, e.g. in British Patents 965,474 and 1,072,956, may also be used as diisocyanates in the process of the invention, as may cyclohexylphenylmethane-4,4'-diisocyanate. Minor proportions of triisocyanates, e.g. benzene-1,3,5-triisocyanate or p,p',p'-triphenylmethanetriisocyanate, may also be present. p-Phenylenediisocyanate, diphenylmethane-4,4'-diisocyanate, naphthylene-1,5-diisocyanate, toluylenediisocyanate, hexamethylenediisocyanate, isophoronediiisocyanate and trimethylhexamethylenediisocyanate are particularly preferred.

The diamines C.1 used in the second stage of method 1 are preferably hydrogenated addition products of primary amines and acrylonitrile, e.g. N-(n-butyl)-propylene-

1,3 - diamine, N - (t - butyl) - propylene - 1,3 - diamine and N - methylpropylene - 1,3 - diamine. In general, any mixed primary and secondary amine of the general formula  
 5  $H_2N-R^3-NHR^4$  may be used, where  $R^3$  is an alkylene radical of 1 to 10 carbon atoms or an aromatic or cycloaliphatic divalent radical of up to 10 carbon atoms and  $R^4$  is an aromatic, cycloaliphatic or aliphatic monovalent radical of up to 20 carbon atoms. Because of the substantial difference in reactivity between the primary and the secondary amino group, the primary amino group reacts preferentially with the isocyanate to give the corresponding aminourea.

Aromatic, aliphatic and cycloaliphatic monoamines, e.g. of up to 13 carbon atoms, may be used as the mono-primary amine C.2 in the second stage of method 2. Examples are methylamine, ethylamine, propylamine, butylamine, 1,4-dimethylpentylamine, tridecylamine, 2-methoxyethylamine, 3-methoxypropylamine, 3 - (2 - ethylhexyloxy) - propylamine, as well as generally analogous 2-alkoxyethylamines and 3-alkoxypropylamines, and also cyclohexylamine, 2-methylcyclohexyl-norbornylamine, benzylamine, 2-phenylethylamine, aniline, o-toluidine, 4 - nitro - 2 - toluidine, and 2,6 - dibromo - 4 - nitroaniline. The amine C.2 may also contain non-primary amino groups, e.g. it may be p-methoxyphenylthiourea, 6 - methoxy - 2 - aminobenzothiazole, 4 - (3 - aminopropyl) - morpholine, 2 - amino - pyrimidine or 1 - (2 - aminoethyl) - piperazine.

The diepoxides D used are, e.g., condensation products of aliphatic or aromatic dialcohols, such as butanediol, hexanediol or neopentylglycol, but preferably bisphenol A, with epichlorohydrin.

The reactions are preferably carried out in solution. Preferably, polar solvents which are inert towards isocyanate groups and which dissolve the polyurethanes produced are employed. Examples of suitable solvents are dimethylformamide, tetrahydrofuran, cyclohexanone, dioxane, ethylglycol acetate and methyl ethyl ketone, but less polar solvents, e.g. toluene or ethyl acetate, may be used together with these.

From the point of view of the subsequent use of the polyurethanes according to the invention in coating compositions, an advantageous average viscosity of the polyurethanes is from 100 to 20,000 cp (in from 15 to 50% by weight strength solution). The viscosity can be adjusted deliberately by chain lengthening, by adding to the solution of the polyurethane minor proportions of bifunctional organic compounds, the nature of which depends on the end groups of the polyurethane, e.g. diepoxides and diisocyanates if secondary amino end groups are present, diamines and diisocyanates if epoxide end groups are present

and amines, epoxides or alcohols if isocyanate end groups are present. The chain-lengthened polyurethane will then have end groups depending not only on the method used for its formation but also on the materials used for chain lengthening. If the polyurethane has isocyanate end groups it is advisable to block these with monofunctional reagents, e.g. alcohols or amines, if chain lengthening is not intended.

The polyurethanes according to the invention may be reacted further with partially blocked diisocyanates, in which case the hydroxyl groups in the side positions react with the non-blocked isocyanate group. By suitably choosing the amount of blocked diisocyanate, the reaction can be directed so that either all or only some of the hydroxyl groups react. It is preferable only to convert about half the hydroxyl groups. The partially blocked diisocyanates are preferably produced from diisocyanates wherein the isocyanate groups differ in reactivity, e.g. toluenediisocyanate, isophoronediiisocyanate or 4,4'-diisocyanatophenyl cyclohexylmethane. Aliphatic diisocyanates, e.g. isophoronediiisocyanate, are particularly suitable for use in light-fast coatings. Suitable blocking agents are the conventional CH—, NH— or OH-acidic compounds, e.g. dialkyl malonates, caprolactam and phenols.

The thermoplastic polyurethanes which carry blocked isocyanate side groups and hydroxyl side groups may be employed directly as self-crosslinking, heat-curable one-component surface coatings. On baking, the blocking agent is eliminated and the isocyanate groups liberated are able to react with the hydroxyl groups, producing crosslinking.

If the thermoplastic polyurethanes of the invention are mixed with completely blocked diisocyanates or higher polyisocyanates, heat-curable one-component surface coatings are again obtained.

The polyurethanes according to the invention may also be used for heat-curable two-component surface coating compositions. In that case, the crosslinking component used as the other component is a polyfunctional organic compound, e.g. a polyisocyanate, a polyepoxide, a melamine resin or a urea resin. Diisocyanates or higher polyisocyanates are preferred and in addition to the above diisocyanates it is also possible to use, e.g., addition products of trimethylolpropane and 3 moles of toluenediisocyanate, the biuret-polyisocyanate obtained from 3 moles of hexamethylenediisocyanate, or an isocyanato-polyisocyanate obtained from 5 moles of toluenediisocyanate.

The coating compositions can contain the conventional additives, e.g. pigments, fillers, flow control agents and solvents. If required, the curing can be accelerated by adding the

65

70

75

80

85

90

95

100

105

110

115

120

125

catalysts conventionally used in isocyanate chemistry.

The coating compositions may be applied as solutions, by brushing, roller-coating, casting or spraying, onto the substrates to be coated, e.g. metal, wood or plastics materials. Curing is generally effected at above 80°C and preferably at from 100 to 180°C.

After curing, the coating compositions give surface coatings which adhere well to the substrates and are furthermore distinguished by great hardness, elasticity, very good resistance to chemicals, high gloss, good weathering resistance and pigmentability.

In the Examples, parts and percentages are by weight.

#### Example 1.

##### a) Preparation of the polyisocyanate:

540 g of polytetrahydrofuran of molecular weight about 2,000 (0.54 equivalent of OH), 65.5 g of neopentylglycol (1.26 equivalents of OH), 279 g of isophoronediiisocyanate (2.52 equivalents of NCO), 600 g of ethylglycol acetate and 0.04 g of dibutyl-tin dilaurate are weighed into a 2 l flask equipped with a stirrer, thermometer and reflux condenser. The mixture is then heated to 80°C in the course of 30 minutes, whilst stirring, and is subsequently stirred for a further 1½ hours at the same temperature. The resulting polyisocyanate contains 2.02% of NCO groups.

##### b) Preparation of the polyurethane:

61.0 g of methylaminopropylamine (1.386 equivalents of amine) and 262 g of ethylglycol acetate are introduced into a 4 l flask; the mixture is then heated to 50°C in the course of 20 minutes, whilst stirring, and the polyisocyanate obtained in a) is added. Finally, 404 g of a 40% strength solution of a reaction product of bisphenol A with epichlorohydrin (0.36 equivalent of epoxide) in ethylglycol acetate and 550 g of ethylglycol acetate are added and the batch is heated to 110°C. After stirring for four hours at this temperature, the reaction mixture is diluted with 922 g of a 1:1 mixture of ethylglycol acetate and dimethylformamide, and the solution is cooled to room temperature and brought to a viscosity of 750 cp by adding about 20 g of isophoronediiisocyanate.

#### Example 2.

##### a) Preparation of the polyisocyanate:

The procedure followed is as in Example 1a), but using the following quantities: 375 g of polytetrahydrofuran (0.375 equivalent of OH), 110 g of neopentylglycol (2.125 equivalents of OH), 388 g of isophoronediiisocyanate (3.5 equivalents of NCO), 600 g of ethylglycol acetate and 0.04 g of dibutyl-tin dilaurate.

The polyisocyanate contains 2.8% of NCO groups.

##### b) Preparation of the polyurethane:

The procedure followed is as in Example 1b), but with the following quantities: 81.5 g of methylaminopropylamine (1.85 equivalents of amine) and 230 g of ethylglycol acetate are first introduced, the polyisocyanate obtained in a) above, 560 g of the 40% strength solution of epoxide in ethylglycol acetate (0.5 equivalent of epoxide) and 590 g of ethylglycol acetate are added, and the mixture is finally diluted with 980 g of ethylglycol acetate.

The viscosity of the solution at room temperature was 720 cp.

#### Example 3.

##### a) Preparation of the polyamine:

73 g of butylamine (1 equivalent of NH<sub>2</sub>) and 263 g of ethylglycol acetate are introduced into a 4 l flask, 190 g of a reaction product of bisphenol A and epichlorohydrin (1 equivalent of epoxide) are then added in the course of one hour, whilst stirring, and the reaction product is subsequently stirred for 2 hours at 80°C.

##### b) Preparation of the polyisocyanate:

490 g of a poly(butanediol adipate) of molecular weight 1,000 (0.98 equivalent of OH), 52 g of neopentylglycol (1 equivalent of OH), 394 g of diphenylmethanediisocyanate (3.152 equivalents of NCO) and 936 g of ethylglycol acetate are weighed into a 2 l flask, heated to 60°C whilst stirring and then stirred for a further 3 hours at the same temperature.

##### c) Preparation of the polyurethane:

The polyisocyanate obtained in b) is added to the polyamine obtained in a) in the course of 2 hours at 40°C, whilst stirring. In the course thereof the viscosity increases and the reaction mixture is therefore diluted in stages to 30%. When the viscosity of the 30% strength solution has reached 1,000 cp at 40°C, the reaction is terminated by adding 20.5 g of dibutylamine, which reacts with the isocyanate end groups. The final viscosity at 22°C is 1,700 cp.

#### Example 4.

1,000 g of the polyurethane from Example 2, which contains about 0.306 equivalent of OH groups in side positions, and 0.1 g of dibutyl-tin dilaurate are heated in a 2 l flask to 40°C, whilst stirring, and 56 g of an addition product of 1.3 moles of caprolactam and 1 mole of isophoronediiisocyanate (0.106 equivalent of NCO) are added in the course of 30 minutes. The reaction mixture is then heated at 60°C. After 4 hours at this temperature, the reaction has ended.

Use Examples.

In each of these Examples, 100 g of the reactive polyurethane solution were mixed with the curing agent shown in Table 1, and a 150  $\mu$  thick layer of the mixture was knife-coated onto iron sheets and cured under the conditions shown in Table 1. Table 2 shows some of the technical properties of the surface coating.

TABLE 1

| Example | Polyurethane   | Curing agent                 | Crosslinking Conditions                     |
|---------|----------------|------------------------------|---|
| 5       | from Example 1 | 6.2 g of biuret-isocyanate ① | 7 days at 23°C                              |
| 6       | from Example 1 | 6.2 g of biuret-isocyanate   | 1 day at 23°C followed by 6 hours at 80°C   |
| 7       | from Example 1 | 8 g of N-adduct ②            | 3 hours at 23°C followed by ½ hour at 160°C |
| 8       | from Example 1 | 5.3 g of I-adduct ③          |   |
| 9       | from Example 2 | 6.2 g of biuret-isocyanate   | 7 days at 23°C                              |
| 10      | from Example 2 | 6.2 g of biuret-isocyanate   | 1 days at 23°C followed by 6 hours at 80°C  |
| 11      | from Example 2 | 8 g of N-adduct ②            | 3 hours at 23°C followed by ½ hour at 160°C |
| 12      | from Example 2 | 6.2 g of I-adduct ③          |   |
| 13      | from Example 4 | —                            | 3 hours at 23°C followed by ½ hour at 160°C |

① : Biuret-isocyanate:  $\text{OCN}-(\text{CH}_2)_6-\text{N} \begin{array}{c} \text{CO}-(\text{CH}_2)_6-\text{NCO} \\ \text{CO}-(\text{CH}_2)_6-\text{NCO} \end{array}$   
75% strength solution in ethyl acetate  
(idealized structure)

② : Biuret-isocyanate ①, blocked with diethyl malonate

③ : Isophorone-diisocyanate, blocked with diethyl malonate

TABLE 2

| Example | König<br>pendulum hardness<br>DIN 53,157,<br>in [sec] | Erichsen<br>deep-drawing value<br>DIN 53,156<br>[mm] | Cross-cut test<br>DIN 53,151 | Solubility<br>in acetone in xylene |
|---------|---|--|------------------------------|------------------------------------|
| 5       | 30  | 12   | 1                            | insoluble insoluble                |
| 6       | 35  | 12   | 1                            | insoluble insoluble                |
| 7       | 36  | 12   | 1                            | insoluble insoluble                |
| 8       | 42  | 12   | 1                            | insoluble insoluble                |
| 9       | 123   | 12   | 1                            | insoluble insoluble                |
| 10      | 132   | 12   | 1                            | insoluble insoluble                |
| 11      | 141   | 12   | 1                            | insoluble insoluble                |
| 12      | 168   | 12   | 1                            | insoluble insoluble                |
| 13      | 162   | 12   | 1                            | insoluble insoluble                |

## WHAT WE CLAIM IS:—

1. A process for the manufacture of a crosslinkable thermoplastic polyurethane which has a molecular weight greater than 1000 and which contains at least two urethane groups, at least two urea groups, at least two tertiary nitrogen atoms, at least two hydroxyl groups in side positions and secondary amino

groups and/or epoxide groups as end groups, which process comprises reacting a polyhydroxy compound A with a diisocyanate compound B in a first stage employing more than 0.5 molecule of diisocyanate B per hydroxyl group in A, reacting the resulting polyisocyanate with a diamine C.1 carrying a primary amino group and a secondary amino

10

15

group in a second stage employing more than 0.5 molecule of diamine C.1 per isocyanate group of the polyisocyanate, and reacting the resulting polyamine with a diepoxide compound D in a third stage employing sufficient diepoxide D to provide from 0.5 to 2 epoxide groups of the diepoxide D per secondary amino group of the polyamine.

2. A process as claimed in claim 1, wherein from 0.6 to 1 molecule of diamine C.1 is employed in the second stage per isocyanate group of the polyisocyanate.

3. A process as claimed in claim 1 or 2, wherein sufficient diepoxide D is employed in the third stage to provide about one epoxide group of the diepoxide D per secondary amino group of the polyamine.

4. A process as claimed in any of claims 1 to 3, wherein the diamine C.1 has the formula  $H_2N-R^3-NHR^4$  where  $R^3$  is an alkylene radical of 1 to 10 carbon atoms or an aromatic or cycloaliphatic divalent radical of up to 10 carbon atoms and  $R^4$  is an aromatic, cycloaliphatic or aliphatic monovalent radical of up to 20 carbon atoms.

5. A process as claimed in claim 4, wherein the diamine C.1 is a hydrogenated addition product of acrylonitrile and a primary amine.

6. A process for the manufacture of a crosslinkable thermoplastic polyurethane which has a molecular weight greater than 1000 and which contains at least two urethane groups, at least two urea groups each including a tertiary nitrogen atom, at least two hydroxyl groups in side positions and secondary amino groups and/or isocyanate groups as end groups, which process comprises reacting a polyhydroxy compound A with a diisocyanate compound B in a first stage employing more than 0.5 molecule of diisocyanate B per hydroxyl group in A, reacting an amine C.2 carrying a single primary amino group with a diepoxide compound D in a second, independent stage employing sufficient amine C.2 to provide about one amino group of the amine C.2 per epoxide group in D, and reacting the polyisocyanate resulting from the first stage with the polyamine resulting from the second stage in a third stage employing sufficient polyisocyanate to provide from 0.5 to 2 isocyanate groups of the polyisocyanate per secondary amino group of the polyamine.

7. A process as claimed in claim 6 wherein sufficient polyisocyanate is employed in the third stage to provide about one isocyanate group of the polyisocyanate per secondary amino group of the polyamine.

8. A process as claimed in claim 6 or 7, wherein the amine C.2 is an aromatic, aliphatic or cycloaliphatic primary monoamine of up to 13 carbon atoms.

9. A process as claimed in any of claims 1 to 8, wherein from 0.6 to 1 molecule of

diisocyanate B is employed in the first stage per hydroxy group of A.

10. A process as claimed in any of claims 1 to 9, wherein the polyhydroxy compound A is a mixture of a polyhydroxy compound having a molecular weight of from 600 to 5,000 and a polyhydroxy compound having a molecular weight below 600.

11. A process as claimed in any of claims 1 to 10, wherein the polyhydroxy compound A comprises a saturated aliphatic or cycloaliphatic diol of up to 6 carbon atoms and/or a hydroxyl-containing saturated polyester or polyether of molecular weight from 800 to 3,000.

12. A process as claimed in any of claims 1 to 11, wherein the diisocyanate B is p-phenylene diisocyanate, diphenylmethane-4,4'-diisocyanate, naphthylene-1,5'-diisocyanate, toluylenediisocyanate, hexamethylenediisocyanate, isophoronediiisocyanate or trimethylhexamethylenediisocyanate.

13. A process as claimed in any of claims 1 to 12, wherein the diepoxide D is a condensation product of an aliphatic or aromatic dialcohol with epichlorohydrin.

14. A process as claimed in any of claims 1 to 13, wherein the reaction stages are carried out in solution in a polar solvent which is inert towards isocyanate groups and which dissolves the polyurethane produced.

15. A process as claimed in any of claims 1 to 14, wherein the polyurethane is subjected to chain lengthening by reaction with a minor proportion of (i) a diepoxide or diisocyanate which reacts with secondary amino end groups if such be present, and/or (ii) a diamine or diisocyanate which reacts with epoxide end groups if such be present, and/or (iii) an amine, epoxide or alcohol which reacts with isocyanate end groups if such be present, the polyurethane produced having end groups depending not only on the reactions used for its initial formation but also on the materials used for chain lengthening.

16. A process as claimed in claim 1 or 6 for the manufacture of a crosslinkable thermoplastic polyurethane carried out substantially as described in any of the foregoing Examples 1 to 3.

17. Crosslinkable thermoplastic polyurethanes when manufactured by a process as claimed in any of claims 1 to 16.

18. Crosslinkable thermoplastic polyurethanes as claimed in claim 17 having a molecular weight of from 5,000 to 100,000 and/or a viscosity of from 100 to 20,000 cP (measured in from 15 to 50% by weight strength solution).

19. A process for the manufacture of a self-crosslinkable thermoplastic polyurethane wherein a polyurethane as claimed in claim 17 or 18 is reacted with a partially blocked

65

70

75

80

85

90

95

100

105

110

115

120

125

diisocyanate, whereby some or all of the hydroxyl groups in side positions react.

- 5 20. The use of a crosslinkable thermoplastic polyurethane manufactured by a process as claimed in claim 19 as a self-crosslinking, heat-curable, one-component surface coating composition.

- 10 21. A process for the manufacture of a heat-curable, one-component surface coating composition, wherein a crosslinkable thermoplastic polyurethane as claimed in claim 17 or 18 is mixed with a completely blocked polyisocyanate.

- 15 22. A process for the formation of a heat-curable surface coating from a two-component composition, wherein a crosslinkable thermoplastic polyurethane as claimed in claim 17 or 18 is used as one component together with a polyfunctional crosslinking agent which

is a polyfunctional organic compound as the other component. 20

23. A process as claimed in claim 22, wherein a polyisocyanate is employed as the polyfunctional crosslinking component.

24. An article or material which has been surface coated with a one-component coating composition as defined in claim 20 or manufactured by a process as claimed in claim 21 or with a coating formed from a two-component coating composition by a process as claimed in claim 22 or 23, followed by curing of the formed surface coating at above 80°C. 25 30

J. Y. & G. W. JOHNSON,  
Furnival House,  
14—18 High Holborn,  
London WC1V 6DE,  
Chartered Patent Agents,  
Agents for the Applicants.